

# Gaia's breath—global methane exhalations

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## Abstract

Methane (CH<sub>4</sub>) is the most abundant organic compound in the Earth's atmosphere, where it acts as a greenhouse gas and thus has implications for global climate change. The current atmospheric CH<sub>4</sub> budget, however, does not take into account geologically-sourced CH<sub>4</sub> seepage. Geological sources of CH<sub>4</sub> include natural macro- and micro-seeps, mud volcanoes, and other miscellaneous sources such as gas hydrates, magmatic volcanoes, geothermal regions, and mid-ocean ridges. Macro-seeps contribute ~25 Tg (teragrams) CH<sub>4</sub>/yr to the atmosphere, whereas, micro-seepage contributes perhaps 7 Tg CH<sub>4</sub>/yr. Mud volcanoes emit ~5 Tg CH<sub>4</sub>/yr, and miscellaneous sources emit ~8 Tg CH<sub>4</sub>/yr to the atmosphere. Thus, the total contribution to the atmosphere from geological sources is estimated to be 45 Tg CH<sub>4</sub>/yr, which is significant to the atmospheric organic carbon cycle and should be included in any global inventory of atmospheric CH<sub>4</sub>. We argue that the atmospheric CH<sub>4</sub> global inventory of the Interplanetary Panel on Climate Change must be adjusted in order to incorporate geologically-sourced CH<sub>4</sub> from naturally occurring seepage.

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*Keywords:* Methane; Seeps; Global inventory; Carbon cycle

## 1. Introduction

The surface of the Earth is the site of fundamental biogeochemical processes involving the release and exchange of various gaseous compounds, such as carbon dioxide (CO<sub>2</sub>) and oxygen (O<sub>2</sub>). Well known is the biological exchange of CO<sub>2</sub> for O<sub>2</sub> by heterotrophic organisms and the counterpart exchange of CO<sub>2</sub> by autotrophic consumption to produce O<sub>2</sub> during photosynthesis in a life-sustaining cycle. Carbon dioxide is also generated by geological processes. It is released at the Earth's surface through volcanism and is the product of O<sub>2</sub>-utilizing combustion of biomass and fossil fuels.

Also present in the atmosphere near the Earth's surface (i.e. in the troposphere) are other gases, including N<sub>2</sub>, H<sub>2</sub>, He, Ar, Rn, CO, SO<sub>2</sub>, H<sub>2</sub>O (vapor), H<sub>2</sub>S, HCl, DMS, CH<sub>3</sub>SH, (CH<sub>3</sub>)<sub>3</sub>N, CH<sub>4</sub> and higher molecular-weight hydrocarbons, all of which are part of the gaseous exhalations from the Earth. In Greek mythology, the Goddess of Earth is named Gaia; thus, one could refer to

the rich mixture of atmospheric gases exhaling at the Earth's surface as Gaia's breath. This analogy might be favored by Lovelock (1995), who formulated the Gaia hypothesis (later called Gaia theory) to explain the workings of the living Earth.

Besides CO<sub>2</sub>, the other principal carbon-containing gas in Gaia's breath is CH<sub>4</sub> (methane), the most abundant organic compound in the Earth's atmosphere. Its total abundance, which is generally increasing slowly (Dlugokencky et al., 1998), is currently approaching 5000 Tg (1 Tg=10<sup>12</sup> g CH<sub>4</sub>), according to IPCC (2001). This organic component of Gaia's breath is the subject of this paper.

The CH<sub>4</sub> atmospheric budget and the sources of CH<sub>4</sub> for this budget have been subjects of increasing interest starting with Ehhalt and Schmidt (1978), and followed by Cicerone and Oremland (1988), Fung et al. (1991), IPCC (1996), Lelieveld et al. (1998), Houweling et al. (1999), and IPCC (2001), and reviewed by Reeburgh (2003). CH<sub>4</sub> plays an important role in the Earth's radiative and chemical balance and thus is a factor in considerations of global climate change (IPCC, 2001). In the estimates of the global CH<sub>4</sub> budget referenced above, the sources can be organized under two main categories, natural (wetlands, termites, oceans, fresh water, wild ruminants, natural forest fires, and gas hydrates)

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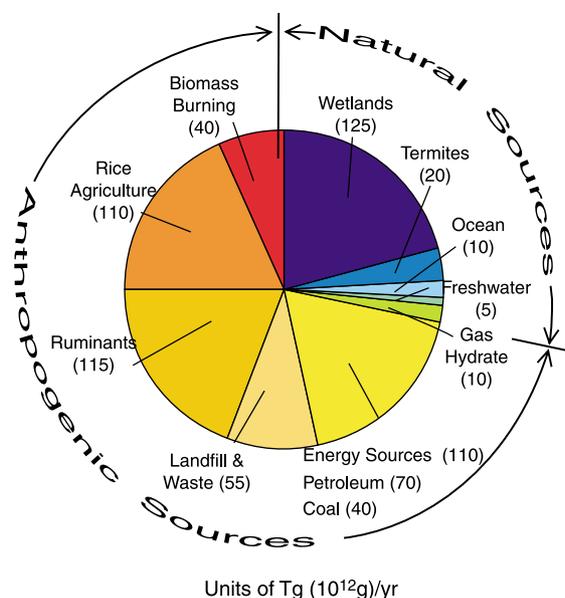


Fig. 1. Diagram showing the relative contributions from various sources to the global atmospheric CH<sub>4</sub> budget. Information obtained from IPCC (2001). Units in Tg (10<sup>12</sup> g) CH<sub>4</sub>/yr.

and anthropogenic (energy use, landfill and waste treatment, domesticated ruminants, rice agriculture, and biomass burning). The total estimated source strength ranges from 500 (Fung et al., 1991) to 600 Tg CH<sub>4</sub>/yr (Lelieveld et al., 1998). IPCC (2001) concluded their Third Assessment Report with a best estimate of 598 Tg CH<sub>4</sub>/yr. Fig. 1 shows the relative contributions of CH<sub>4</sub> to the atmospheric budget from the various identified sources. Although it is recognized that there are probable errors in the estimated contributions from each of the various sources, for the purpose of this paper, the relative proportion of each contributing source and the total flux of 600 Tg CH<sub>4</sub>/yr are considered to be correct, given the present state of knowledge. However, it will be argued that one of the contributing sources needs to be adjusted to account for naturally occurring CH<sub>4</sub> seepage in Gaia's breath.

Most of these sources in the global CH<sub>4</sub> budget result from active biological processes. Biomass burning and natural forest fires, in which biological materials are incompletely combusted to yield CH<sub>4</sub> along with the major product CO<sub>2</sub>, is an exception. Even the CH<sub>4</sub> from gas hydrates is mainly produced micro-biologically (Kvenvolden, 1995). Only in the source identified in Fig. 1 as 'energy sources' where fossil fuel is exploited, is the CH<sub>4</sub> non-active biological, i.e. geological, in origin. The energy source is divided into two activities, coal mining and natural gas and crude oil exploitation. These anthropogenic activities produce fossil or old CH<sub>4</sub> that has been generated in the geological past by thermal processes acting on ancient biological materials.

From the geological perspective, however, there are many natural sources of fossil CH<sub>4</sub> that have been

completely ignored in these assessments of the global methane budget, as summarized in IPCC (2001). These natural sources of fossil CH<sub>4</sub> include macro-seeps and mud volcanoes, all found in both terrestrial and submarine settings around the world. In addition, micro-seepage of CH<sub>4</sub> likely occurs globally at the surface of sedimentary basins where petroleum (crude and natural gas) was generated.

The purposes of this paper are to (1) summarize information on the geological sources of CH<sub>4</sub>, (2) estimate their source strengths (annual rates of CH<sub>4</sub> release), and (3) adjust the global methane budget to reflect the contributions of geologically sourced fossil CH<sub>4</sub>. In the discussion that follows, average budget numbers are reported for simplicity, but it should be understood that a range of values is always implied.

## 2. Fate of CH<sub>4</sub>

Atmospheric CH<sub>4</sub> is a moderately reactive trace gas with a current lifetime in the atmosphere of ~7.9 years (Lelieveld et al., 1998). Although low in concentration, it is nevertheless the most abundant organic compound in the atmosphere. It is radiatively significant, functioning as a 'greenhouse gas'. The greenhouse effect of one molecule of CH<sub>4</sub> in the atmosphere is ~25 times that of a molecule of CO<sub>2</sub> (Lelieveld et al., 1998). Most CH<sub>4</sub> is removed from the atmosphere through oxidation by hydroxyl radicals (OH) in the troposphere; further destruction takes place in the stratosphere (Levy, 1971). At the Earth's surface, atmospheric CH<sub>4</sub> diffuses into soils and is subsequently oxidized (Born et al., 1990). Microbial oxidation processes in the Earth also intercept and remove more than 50% of the CH<sub>4</sub> before it reaches the atmosphere (Reeburgh, 2003). Microbial oxidation is particularly effective in the oceans (Reeburgh et al., 1993), and it has also a substantial effect on CH<sub>4</sub> emissions from wetlands, rice production, landfills, and leaks from methane distribution systems, such as pipelines (summarized in Reeburgh, 2003).

Although the total global source strength for CH<sub>4</sub> is 598 Tg CH<sub>4</sub>/yr, the total global sink of CH<sub>4</sub> is 576 Tg CH<sub>4</sub>/yr (IPCC, 2001); the imbalance of 22 Tg CH<sub>4</sub> is added to the atmosphere each year. Atmospheric CH<sub>4</sub> concentrations have increased over time at variable rates. For example, during the last glacial period the concentration was ~0.35 ppm. This amount increased to ~0.75 ppm by 1850 at which time the CH<sub>4</sub> concentration increased much more rapidly as a result of agricultural expansion and industrialization (Lelieveld et al., 1998). By 1998, the globally averaged atmospheric surface abundance of CH<sub>4</sub> was 1.745 ppm, corresponding to a total burden of ~4850 Tg CH<sub>4</sub> (ICPP, 2001).

The atmosphere contains CH<sub>4</sub> that has survived both microbial oxidation in the Earth and hydroxyl radical oxidation in the atmosphere. This residual atmospheric CH<sub>4</sub>

originally comes from the alteration of organic matter on Earth by two distinct processes, one biologically mediated and the other geologically controlled. Microbial CH<sub>4</sub>, often called biogenic CH<sub>4</sub>, is produced by methanogenic archaea as an end product of the decomposition of organic matter involving consortia of diverse micro-organisms. According to IPCC (2001), ~80% of the CH<sub>4</sub> in the atmosphere results from present or past methanogenic activity and ~20% is 'old' or 'fossil' and comes originally from the thermal decomposition of organic matter. This thermogenic CH<sub>4</sub> (and other hydrocarbon gases) is formed from the thermal breakdown of complex organic compounds, including kerogen, at high pressures and temperatures ( $\geq 80$  °C) at depths in excess of ~1 km below the Earth's surface (Judd et al., 2002). A third, but minor category of CH<sub>4</sub> is abiogenic CH<sub>4</sub>, derived by inorganic processes operating deep within the Earth's crust and underlying mantle; the amount of abiogenic CH<sub>4</sub> reaching the Earth's surface and entering the atmosphere is likely very small (Welhan and Craig, 1983).

### 3. Isotopic constraints on atmospheric CH<sub>4</sub>

Microbial, thermogenic, and abiogenic CH<sub>4</sub> originates on Earth with each category having distinctive ranges of carbon isotopic ( $\delta^{13}\text{C}$ ) compositions which are not absolute but are useful for classification: microbial, mainly between  $-60$  and  $-70\text{‰}$ , with values ranging to as light as  $-110\text{‰}$ ; thermogenic, generally from  $-20$  to  $-52\text{‰}$ ; and abiogenic, ranging from about  $-5$  to  $-45\text{‰}$ , reported relative to the PeeDee Belemnite Standard (summarized by Judd, 2000). These initial carbon isotopic signatures are partially fractionated by processes of oxidation as the CH<sub>4</sub> escapes from the Earth's surface. Methane that survives is isotopically enriched in  $^{13}\text{C}$ . Microbial methane oxidation, both anaerobic and aerobic, is estimated to consume over half of the total methane produced on Earth. In fact, anaerobic methane oxidation is nearly a quantitative sink for CH<sub>4</sub> diffusing from anoxic oceanic sediments (Reeburgh et al., 1993). Aerobic oxidation takes place in the oceanic water column, and rates of oxidation have been measured by observing decreases in CH<sub>4</sub> concentrations (Scranton and Brewer, 1978) and by direct tracer studies (Reeburgh et al., 1991; Valentine et al., 2001). Not only does CH<sub>4</sub> undergo carbon isotopic fractionation in sediments and oceans, it is also isotopically fractionated in the atmosphere by hydroxyl radical oxidation (summarized in Fung et al., 1991). The end result is that the mean stable carbon isotopic composition ( $\delta^{13}\text{C}$ ) of atmospheric CH<sub>4</sub>, as measured for 1990–1995, is  $-47.3\text{‰}$  (Quay et al., 1999).

The  $^{14}\text{C}$  content of atmospheric CH<sub>4</sub> has also been used to constrain the global CH<sub>4</sub> budget. Radiocarbon ( $^{14}\text{C}$ ) is only present in CH<sub>4</sub> produced from modern (<35,000 yr old) organic carbon by biogenic processes. Methane from thermogenic processes results from old organic carbon containing no  $^{14}\text{C}$ . Thus, the fraction of  $^{14}\text{C}$  in the increasing amount of CH<sub>4</sub>

in the atmosphere is believed to be sensitive to fossil fuel-related CH<sub>4</sub> emissions, because the 'old' CH<sub>4</sub> from geological deposits is depleted in  $^{14}\text{C}$  (Lelieveld et al., 1998). If the relative contribution from fossil fuel-related CH<sub>4</sub> sources (energy sources in Fig. 1) can be estimated from  $^{14}\text{CH}_4/^{12}\text{CH}_4$  measurements in the atmosphere, then 18% of atmospheric CH<sub>4</sub> is from fossil-fuel energy sources and the remaining 82% is from microbial processes (IPCC, 2001).

### 4. Natural methane emissions

The total source strength of the CH<sub>4</sub> budget is about 600 Tg CH<sub>4</sub>/yr (Fig. 1), and ~18% of the CH<sub>4</sub>, or ~110 Tg CH<sub>4</sub>/yr contains  $^{14}\text{C}$  depleted carbon (IPCC, 2001). While all of this fossil CH<sub>4</sub> is currently attributed to the exploitation of fossil fuels, some must also result from natural processes that continuously emit CH<sub>4</sub> to the atmosphere as a part of Gaia's breath. These CH<sub>4</sub> emissions are all natural gas seeps, and they include macro-seeps, which have visible manifestations, such as bubbles when the seeps are under water, and micro-seeps, which are invisible and usually are detected by chemical measurements. Mud volcanoes are a special category of macro-seeps; the exits of these natural seeps are volcano-like in appearance. Gas hydrate, a solid form of CH<sub>4</sub> and water, is often associated with macro-seeps, including mud volcanoes, which occur in very deep water. Gas hydrate is considered a manifestation of natural gas seepage under special circumstances.

#### 4.1. Natural macro-seeps

Natural seepages of petroleum (crude oil and natural gas) are globally widespread (Fig. 2) in both terrestrial and marine environments (Wilson et al., 1973, 1974). Their occurrences have been documented since the beginning of recorded history. For example, there are biblical references to very heavy crude oil (asphalt) seeps around the Dead Sea, and burning gas (methane) seeps in the Baku region of Azerbaijan were sites of fire-worship by early Zoroastrian religious groups (Levorsen, 1956).

Oil seeps commonly entrain gas, and gas seepages are often accompanied by some crude oil. Because of the close association between oil and gas seeps, it is possible to estimate the amount of gas escaping from the surface of the Earth based on estimates of the global seepage of crude oil and a global gas/oil ratio.

A study from the US National Academy of Sciences (NAS, 2003) concludes that, as a best estimate,  $\sim 6 \times 10^5$  ton (1 ton =  $10^6$  g)/yr of crude oil seep into the marine environment. Details leading to this estimated global crude oil seepage rate are given in Kvenvolden and Cooper (2003). A summary of gas/oil ratios (GOR) for 141 petroleum systems of the world shows that 126 of these systems have both oil and gas, assumed to be mainly CH<sub>4</sub>,

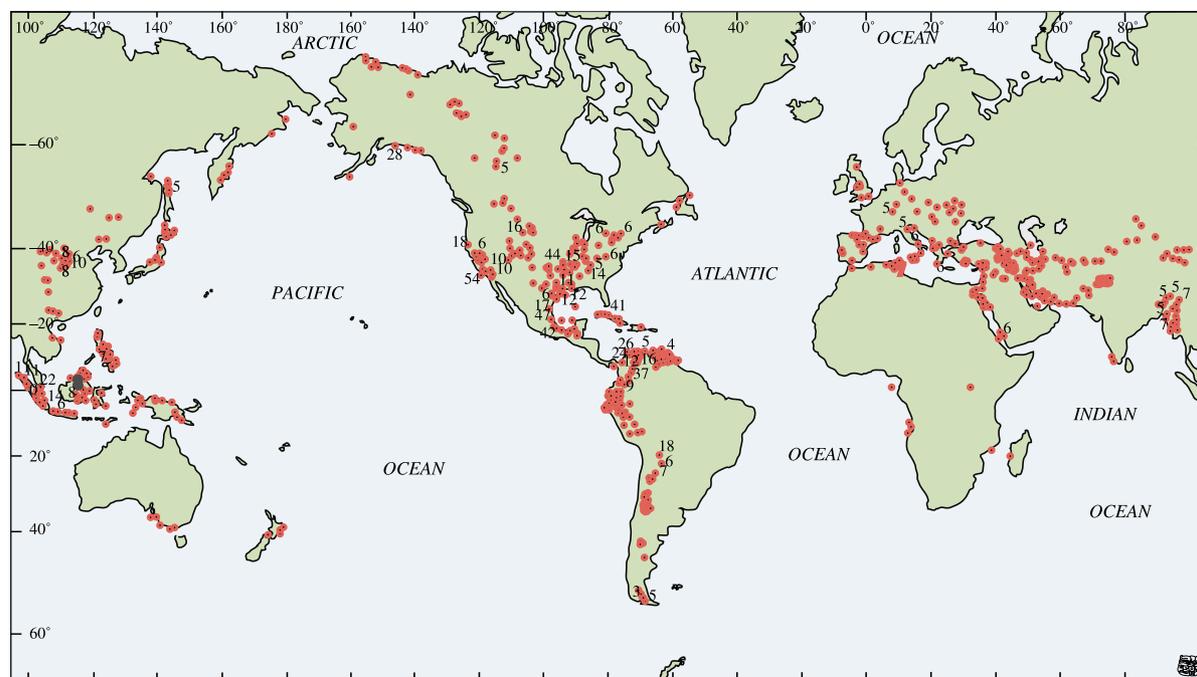


Fig. 2. Map showing the global distribution of onshore and offshore oil seeps many of which also emit natural gas. Numbers indicate the count of seeps in a given region. Redrawn and modified from Wilson et al. (1973, 1974).

whereas 12 of them produce only gas, and three produce only crude oil (Peters et al., 2005, p. 756). The average GOR of the 126 petroleum systems is  $2.3 \times 10^5$ . Assuming that the  $6 \times 10^5$  ton of crude oil seeping into the marine environment each year has this average GOR, then the amount of  $\text{CH}_4$  seepage into the oceans is  $\sim 20$  Tg/yr. This estimate is conservative in that no contribution from the 12 gas-only petroleum systems is considered here, and no loss factor in the water column is included. Assuming further that submarine gas seeps are restricted to continental margins and that terrestrial gas seeps found in areas of comparable extent, gas seeps on land may emit directly to the atmosphere an equivalent amount of  $\text{CH}_4$ , or 20 Tg. Thus, the total global flux from natural seeps is estimated to be  $\sim 40$  Tg  $\text{CH}_4$ /yr.

Of interest is a comparison of this estimate of 40 Tg  $\text{CH}_4$ /yr with previously published estimates by various authors. For example, Ehhalt and Schmidt (1978) calculated the global oceanic flux of  $\text{CH}_4$  to the atmosphere based on the rate of molecular diffusion of  $\text{CH}_4$  through the air–sea boundary. Trotsyuk and Avilov (1988) measured the disseminated flux of  $\text{CH}_4$  in the Black Sea and extrapolated these results worldwide to obtain a global estimate of seafloor  $\text{CH}_4$  emissions. Hovland et al. (1993) used published estimates of seafloor flux and seepage distributions to determine a global seafloor flux for  $\text{CH}_4$ . Cranston (1994) considered  $\text{CH}_4$  release from coastal and marine sediments to estimate the amount of  $\text{CH}_4$  entering the atmosphere from these sources. Observations of the ‘world’s most spectacular

marine hydrocarbon seeps’ offshore from Coal Oil Point, California, by Hornafius et al. (1999) were extrapolated to obtain a  $\text{CH}_4$  flux to the atmosphere. These and other estimations have been compiled by Judd (2000) and Judd et al. (2002). Table 1 summarizes the estimates of  $\text{CH}_4$  emissions from natural seeps in the oceans. As might be expected, these estimates vary, but the results suggest that  $\sim 50$  Tg  $\text{CH}_4$ /yr seeps naturally from the seafloor, based mainly on the estimates of Hovland et al. (1993). About 30 Tg  $\text{CH}_4$ /yr reaches the atmosphere, and 20 Tg  $\text{CH}_4$ /yr is dissolved or converted to  $\text{CO}_2$  by oxidation in the water column.

Another approach to estimating global seepage rates of  $\text{CH}_4$  was attempted at a workshop (where the term ‘Gaia’s

Table 1  
Global estimates of  $\text{CH}_4$  emissions from natural seeps in the oceans

Location	Flux (Tg $\text{CH}_4$ /yr)	Reference
<i>Atmospheric <math>\text{CH}_4</math></i>		
World oceans	1.3–16.6	Ehhalt and Schmidt (1978)
Global	$17 \pm 14$	Lacroix (1993)
Ocean sediments	1–10	Cranston (1994)
Continental shelves	18–48	Hornafius et al. (1999)
Global marine seeps	0.4–12.2	Judd (2000)
<i>Marine <math>\text{CH}_4</math></i>		
Continental shelves	1.9	Trotsyuk and Avilov (1988)
Continental shelves	8–65	Hovland et al. (1993)

Adapted from Judd et al. (2002).

breath' for CH<sub>4</sub> natural seepage was first coined), sponsored by the US Geological Survey, and held in Portland, Oregon, May 2–4, 2001 (Kvenvolden et al., 2001). This approach involved broad assumptions based on considerations of the availability of CH<sub>4</sub> for seepage from all global geological sources through geologic time. The method used was adopted from previous work dealing with global estimates of crude oil seepage (Kvenvolden and Harbaugh, 1983; Miller, 1992). The total reservoir of CH<sub>4</sub> was estimated to be between 10<sup>4</sup> and 10<sup>8</sup> Tg and the half-life of this reservoir was set at 10<sup>8</sup> yr. If the length of time for reservoir depletion is assumed to be 10<sup>8</sup>–10<sup>12</sup> yr—a range broad enough to include all eventualities—then the flux of CH<sub>4</sub> is estimated to be ~30 Tg CH<sub>4</sub>/yr from the seafloor and ~10 Tg CH<sub>4</sub>/yr into the atmosphere. Therefore, estimates of the global CH<sub>4</sub> flux, based on gas/oil ratios, literature surveys, and theoretical considerations, average ~25 Tg CH<sub>4</sub>/yr to the atmosphere and ~35 Tg CH<sub>4</sub>/yr to the seafloor.

In natural hydrocarbon seeps, CH<sub>4</sub> is the major constituent, but gas seeps at the Earth's surface can emit other gases. Thus, Gaia's breath can be complex, and chemical analyses are required to identify seep-gas compositions. Two examples illustrate this point. In Norton Sound, Alaska, a natural gas seep in 20 m of water emits a continuous stream of bubbles. When first discovered and analyzed (Cline and Holmes, 1977), it was reported to be a hydrocarbon gas seep dominated by CH<sub>4</sub>. Later work by Kvenvolden et al. (1979) demonstrated that the natural gas emissions at this seep were dominated by CO<sub>2</sub>, and that hydrocarbon gases, including CH<sub>4</sub>, were only minor constituents. A second example is in northwestern Wyoming where Kvenvolden et al. (1989) observed that in Yellowstone National Park the gas seeps are, like the seep in Norton Sound, dominated by CO<sub>2</sub> with CH<sub>4</sub> as a minor constituent. To the south in Grand Teton National Park, the situation is quite different. Here, the natural seeps are either dominated by CH<sub>4</sub> or by N<sub>2</sub>. These examples show that when trains of bubbles in water indicate the presence of a natural gas seep, chemical analyses are needed to describe the composition of the escaping gas. In all hydrocarbon seeps, however, CH<sub>4</sub> is the dominant component.

#### 4.2. Mud volcanoes

Mud volcanoes are a spectacular manifestation of natural gas seepage at the Earth's surface. They are geologic structures formed as a result of the emission of gas, usually CH<sub>4</sub>, water, and mud at the terrestrial surface and at the seafloor (Dimitrov, 2002). Often included in the mud are angular and rounded rock clasts, ranging in size from a few millimeters to 10 m or more. The clasts may be of various lithologic types and are derived from the walls of the conduits through which the gas–water–mud mixture has passed on its way to the surface. Mud volcanoes are morphologically diverse, ranging from semi-symmetrical mound shapes rising several hundred meters above

the adjacent country-side to regular and irregular conical shapes. Mud volcanoes vary in size from small landforms of less than a meter in diameter to large structures occupying more than 100 km<sup>2</sup>. Eruptions at mud volcanoes may be gentle or violent. In gentle eruptions, the mud volcanoes expand by gradual and progressive outflows of liquid mud. In violent eruptions, mud and mud breccia may shoot up in the air to heights of a few kilometers. The emitted gas may ignite to produce spectacular flames. Fig. 3 shows a typical mud volcano vent at the currently quiescent Dashgil mud volcano complex in Azerbaijan that has been described in detail by Hovland et al. (1997). Azerbaijan is the world capitol of mud volcanoes with ~400 examples located within the South Caspian oil and gas basin and more than 300 mud volcanoes located onshore of eastern Azerbaijan and offshore in the adjacent Caspian Sea (Aliyev et al., 2002).

Mud volcanoes are globally distributed and occur in both the terrestrial and marine environments (Fig. 4). The number of prominent individual mud volcanoes totals ~1950 (Dimitrov, 2003), although the count remains uncertain. For example, Milkov (2000), in an unsubstantiated claim, estimates the number of known and inferred deep-water mud volcanoes to range from 10<sup>3</sup> to 10<sup>5</sup> and chooses the number 5 × 10<sup>3</sup> for the purpose of extrapolating CH<sub>4</sub> flux. Mud volcanoes are irregularly clustered in belts that generally coincide with areas of active plate boundaries and zones of young orogenic activity (Dimitrov, 2002). More than half of the total number of mud volcanoes are located along the Alpine–Himalayan Active Belt where there are ~650 terrestrial and at least 470 offshore prominent examples (Fig. 4). The largest and most active mud volcanoes can be found along this Belt.

Interest in mud volcanoes has recently increased because, in part, their emissions may have implications for global climate change. Dimitrov (2002) provides a comprehensive review of mud volcano occurrence, plumbing systems, and possible geologic consequences. In addition, there are recent reports of mud volcanoes in the Gulf of Mexico (MacDonald et al., 2000), offshore Nigeria (Graue, 2000), South Caspian Sea (Voitov, 2001), Southwest African continental margin (Ben-Avraham et al., 2002), northern Apennines of Italy (Capozzi and Picotti, 2002), Sicily (Etiope et al., 2002), western Mediterranean Sea (Sautkin et al., 2003), Atlantic margin of Morocco (Mazurenko et al., 2003), Gulf of Cadiz (Pinheiro et al., 2003), eastern Romania (Etiope et al., 2004), and East China Sea (Yin et al., 2003). A new mud volcano eruption in New Zealand (Pettinga, 2003) has replaced a hydrocarbon gas seep first described geochemically by Kvenvolden and Pettinga (1989). This example demonstrates quite well that mud volcanoes are a special form of natural-gas seepage at the Earth's surface.

Table 2 summarizes estimates of CH<sub>4</sub> emissions from mud volcanoes. The global flux of CH<sub>4</sub> from mud volcanoes was estimated to be 10.3–12.6 Tg CH<sub>4</sub>/yr by



Fig. 3. Photograph of a mud-volcano vent at the Dashgil mud volcano complex near Baku, Azerbaijan. Photo taken by K.A. Kvenvolden in 2002.

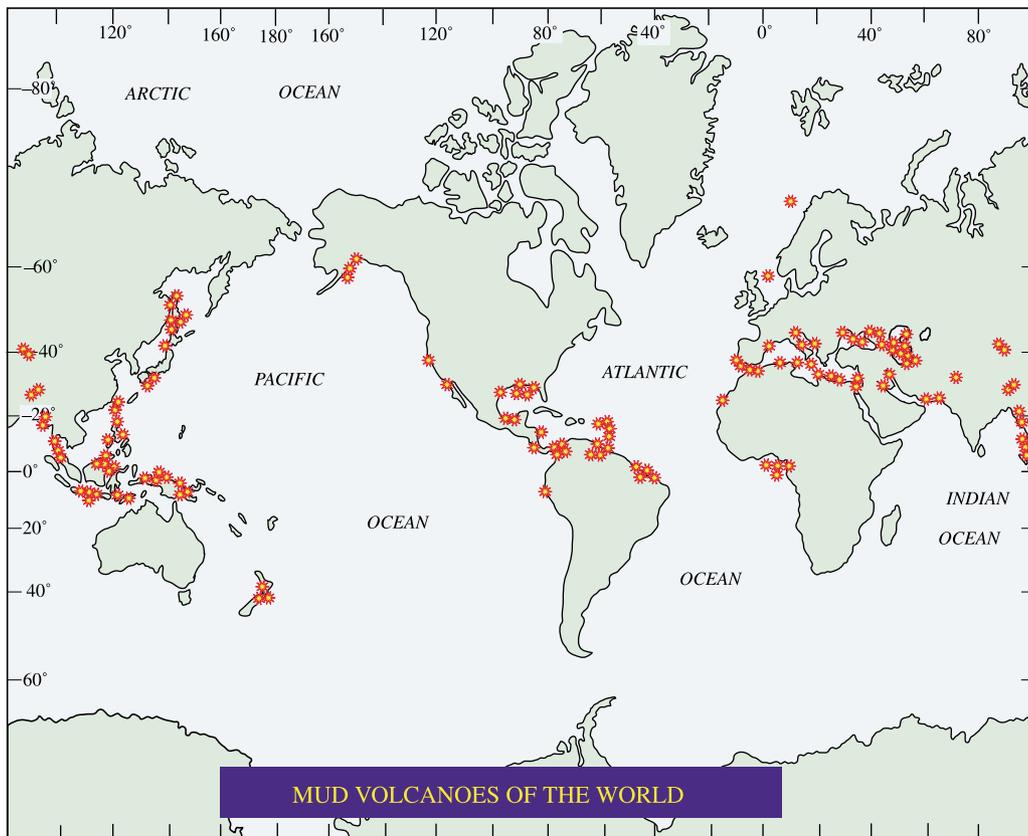


Fig. 4. Map showing the global distribution of onshore and offshore mud volcanoes. Redrawn and modified from Dimitrov (2002).

Table 2  
Estimates of CH<sub>4</sub> emissions from mud volcanoes during quiescent and eruptive phases

Location	Flux (Tg CH <sub>4</sub> /yr)	Reference
Azerbaijan	0.061	Sokolov et al. (1969)
Azerbaijan	0.2	Jakubov et al. (1971)
Azerbaijan	0.014	Guliyev and Feizullayev (1996)
Azerbaijan	0.125	Valyayev (1998)
Global (total)	10.3–12.6	Dimitrov (2002)
Global (atmosphere)	5	Dimitrov (2003)
Global (total)	30.5	Milkov et al. (2002)
Global (atmosphere)	5.5	Milkov et al. (2002)

Adapted from Dimitrov (2002) and modified from Judd et al. (2002).

Dimitrov (2002), who revise the estimate to 5.06 Tg CH<sub>4</sub>/yr (Dimitrov, 2003) to reflect the amount of CH<sub>4</sub> that actually reaches the atmosphere. Milkov et al. (2002) independently estimated the total flux from mud volcanoes to be 30.5 Tg CH<sub>4</sub>/yr with 5.5 Tg CH<sub>4</sub>/yr going into the atmosphere. Given the current understanding of mud volcanoes, a reasonable and conservative estimate of the mud volcano emissions to the atmosphere is about 5 Tg CH<sub>4</sub>/yr.

#### 4.3. Gas hydrate

Gas hydrate is an intermediate storage system for CH<sub>4</sub> that is moving through the plumbing of sediments which lie mainly beneath deep waters (depths greater than ~300 m).

A very large amount of CH<sub>4</sub>, perhaps  $21 \times 10^{15} \text{ m}^3$ , is deposited in gas hydrate (Kvenvolden, 1988a), and because the gas-hydrate reservoir is metastable and dynamic, CH<sub>4</sub> is added to and withdrawn from gas hydrates over geologic time. Gas hydrate is essentially a water clathrate (cage structure) of natural gas (mainly CH<sub>4</sub>) and can be referred to as a methane clathrate hydrate or methane hydrate. The CH<sub>4</sub> in gas hydrate is mainly microbially generated; however, thermogenic CH<sub>4</sub> occurs in gas hydrate of the Gulf of Mexico, the Caspian Sea, and a few other places where there are known petroleum systems (Kvenvolden, 1995). The occurrence of natural gas hydrate is controlled by an interrelation among factors of temperature, pressure, and constituent composition. Because of these factors the occurrence of gas hydrate on Earth is restricted to sediments in polar and deep oceanic regions. In polar regions, gas hydrate is normally associated with permafrost both onshore in continental sediment and offshore in sediment of the continental shelves. In deep oceanic regions, gas hydrate is found in outer continental margins in sediment of slopes and rises where cold bottom water is present (Kvenvolden, 1993). The worldwide occurrence of known and inferred gas hydrate is shown in Fig. 5.

Methane in deep-water natural gas seeps and in deep-water mud volcanoes is commonly present in the form of gas hydrate. For example, in the Gulf of Mexico, gas hydrate breaches the seafloor at sites of gas seepage (MacDonald et al., 1994). Likewise, at Hydrate Ridge on

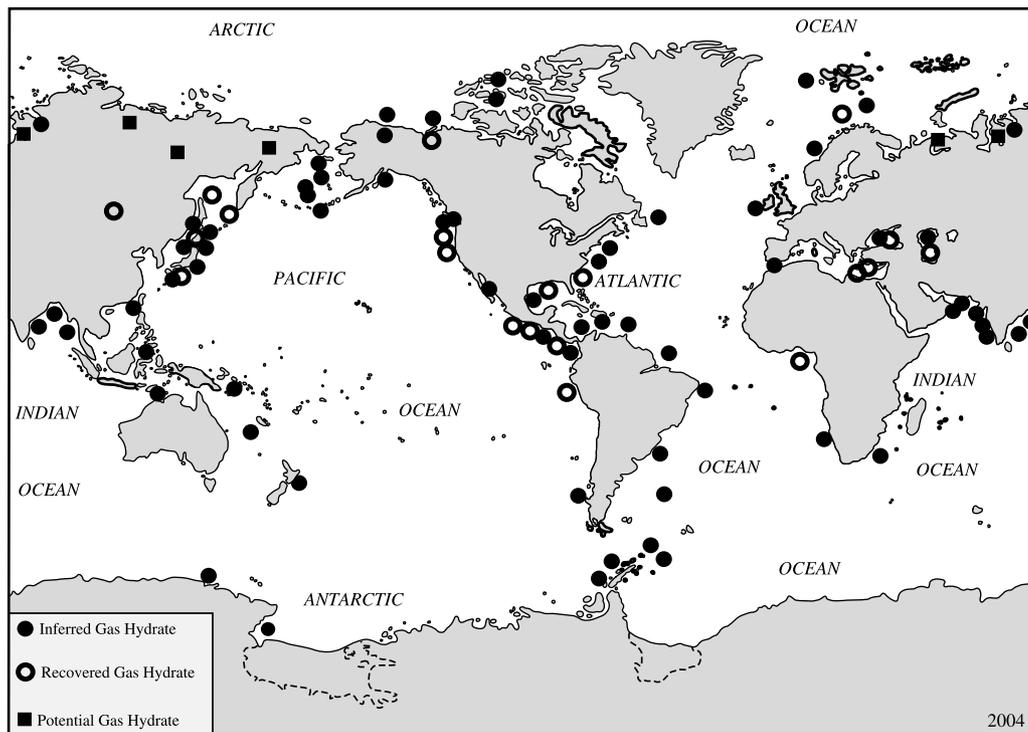


Fig. 5. Map showing worldwide locations of known and inferred gas hydrate in aquatic (oceans, seas, lakes) sediment and in polar continental sediment. Open circles indicate locations where samples of natural gas hydrate have been recovered. Filled circles indicate locations of inferred of gas hydrate. Filled squares are in regions for potential gas-hydrate occurrence in Russia. Adapted from Kvenvolden (2002).

the Cascadia Margin, offshore from Oregon, gas hydrate releases  $\text{CH}_4$  into the water column (Suess et al., 1999). An example of gas hydrate associated with a mud volcano is at the Håkon Mosby mud volcano located on the Norway-Barents-Svalbard margin in the Norwegian Sea (Ginsburg et al., 1999). In each of these gas-hydrate occurrences, there is little evidence that the  $\text{CH}_4$  from the dissociating gas hydrate ever reaches the atmosphere. For example in the Gulf of Mexico, the main source of atmospheric  $\text{CH}_4$  appears to be the prolific subsurface petroleum system rather than the decomposing gas hydrate (Sassen et al., 2001). At Hydrate Ridge, the emission of  $\text{CH}_4$  to the atmosphere is attributed to coastal upwelling rather than to gas hydrate (Rehder et al., 2002). Bubble plumes of  $\text{CH}_4$  from gas hydrate were mapped acoustically and none of the plumes reached the sea surface, although some  $\text{CH}_4$  may have reached the atmosphere from plumes that approached close to the sea surface. At the Håkon Mosby mud volcano, the gas-hydrate  $\text{CH}_4$  is diluted and mixed with the background  $\text{CH}_4$  within the bottom water and is lost to the deep polar Arctic Ocean (Damm and Budéus, 2003).

Although there is little direct, naturally-occurring evidence linking  $\text{CH}_4$  from gas hydrate with the atmosphere, theoretical considerations (Zhang, 2003), empirical experiments (Brewer et al., 2002), and geological reasoning (Kvenvolden, 1988b) provide suggestive evidence that some  $\text{CH}_4$  from gas hydrate may reach the atmosphere. Unanswered questions are: how rapidly do gas hydrates decompose and how effectively is the  $\text{CH}_4$  oxidized? Until the fate of  $\text{CH}_4$  from gas hydrate is fully understood, the present conservative conclusion is that little gas-hydrate  $\text{CH}_4$  ever enters the atmosphere unless there are catastrophic releases wherein significant  $\text{CH}_4$  survives and reaches the atmosphere. There is evidence that  $\text{CH}_4$  from massive

dissociation of gas hydrate has at least entered the oceans in the past as demonstrated by Dickens et al. (1995).

Large amounts of  $\text{CH}_4$  are presently stored in gas hydrate. A ‘consensus estimate’ of  $\sim 10$  Tton (1 Tton =  $10^{18}$  g) of  $\text{CH}_4$  carbon or  $\sim 13$  Tton of  $\text{CH}_4$  has been given (Kvenvolden, 1999), but only a small fraction is believed by some to leak and reach the atmosphere (Lelieveld et al., 1998). Early work by Kvenvolden (1988b) suggested that the amount of leaking  $\text{CH}_4$  is less than 0.12 Tg/yr, later reconsidered to  $\sim 4$  Tg/yr (Kvenvolden, 1991). Cicerone and Oremland (1988) suggested 5 Tg/yr, and IPCC (2001) indicated 10 Tg/yr. These values are all uncertain and, in the case of Cicerone and Oremland (1988), the estimate of 5 Tg  $\text{CH}_4$ /yr is a ‘placeholder’ awaiting verification.

#### 4.4. Micro-seeps of natural gas

One basis for surface prospecting for subsurface petroleum accumulations is the concept of micro-seepage of natural gas (Philp and Crisp, 1982). That is, by measuring the gaseous anomalies resulting from leakage to the Earth’s surface, an assessment can be made of the petroleum potential of a given area (Schumacher and Abrams, 1996). Although surface prospecting has had varying degrees of success over the years, it has also been received with varying levels of skepticism as a petroleum-finding tool (Hunt et al., 2002). Nevertheless, there is no doubt that micro-seepage of  $\text{CH}_4$  does occur, particularly associated with faults and fractures that reach the surface.

Micro-seepage of  $\text{CH}_4$  from ancient sedimentary basins on land (Fig. 6) has been considered by Etiope and Klusman (2002). Micro-seepage involves the slow, continual loss of hydrocarbon gases, including  $\text{CH}_4$ , from

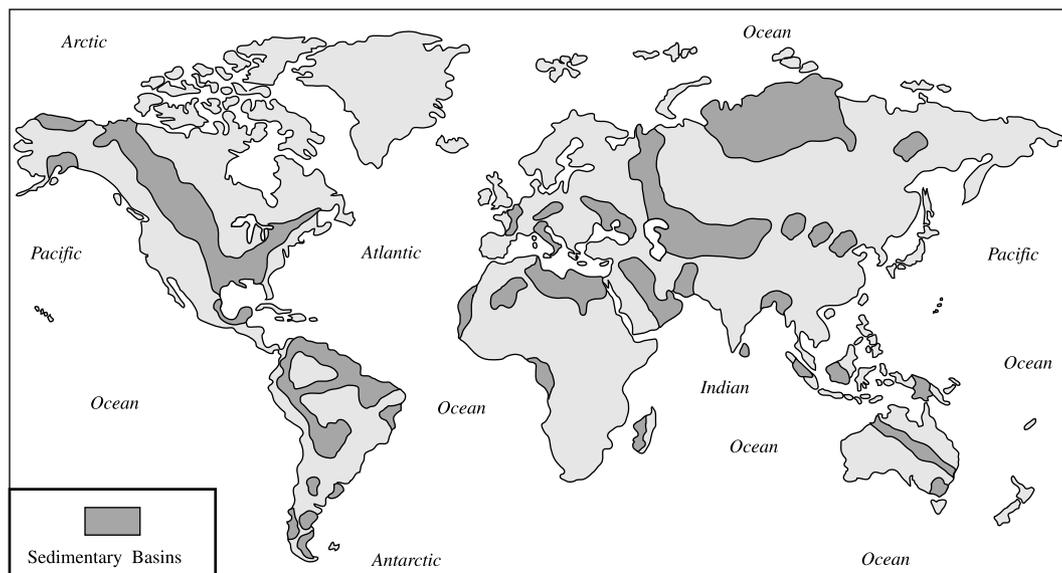


Fig. 6. Map showing location of sedimentary basins throughout the world where micro-seepage of  $\text{CH}_4$  may occur. Adapted from Etiope and Klusman (2002).

depths of as much as 5 km where thermal degradation of organic matter is occurring. Klusman and Jakel (1998) provide an example of natural micro-seepage of CH<sub>4</sub> to the atmosphere in a sedimentary basin with active petroleum exploitation, the Denver–Julesburg Basin of Colorado. Flux data from micro-seepage in hydrocarbon-prone areas often show negative values, depending on season; that is, the area acts as a net sink for CH<sub>4</sub> rather than a net source. Etiope and Klusman (2002), extrapolating from the few available data, estimate the total CH<sub>4</sub> flux from present day land-based sedimentary basins of the world (Fig. 6) to be 70 Tg/yr. This total flux value is reduced, however, to ~7 Tg CH<sub>4</sub>/yr due to the 90% methanotrophic consumption (net sink) of CH<sub>4</sub> that occurs in the soils of the sedimentary basins during the micro-seepage process (Etiope and Klusman, 2002).

CH<sub>4</sub> release through micrseepage is subtle, whereas, CH<sub>4</sub> emissions from mud volcanoes are blatant. Thus, the similarity of the total flux rates from the two phenomena (5 Tg CH<sub>4</sub>/yr for mud volcanoes and 7 Tg CH<sub>4</sub>/yr for micro-seeps) is somewhat surprising. Mud volcanoes have been studied more extensively from a global perspective than have micro-seeps. Thus, the 5 Tg CH<sub>4</sub>/yr global flux is considered to be better constrained than the 7 Tg CH<sub>4</sub>/yr global flux estimated for micro-seeps.

#### 4.5. Miscellaneous sources of CH<sub>4</sub>

There are other sources of CH<sub>4</sub> to the atmosphere besides macro- and micro-seeps and mud volcanoes, and many of these sources are summarized in Judd et al. (2002). For example, although CO<sub>2</sub> is the principal carbon-containing gas released from magmatic volcanoes (not mud volcanoes), the amount of CH<sub>4</sub> released by volcanic activity on land is estimated to be between 0.8 and 6.2 Tg/yr (Lacroix, 1993) or on average ~4 Tg CH<sub>4</sub>/yr. Geothermal areas also emit CH<sub>4</sub> to the atmosphere. Global flux estimates range from 0.9 to 3.2 Tg CH<sub>4</sub>/yr (Lacroix, 1993) and 2.5–6.3 Tg CH<sub>4</sub>/yr (Etiope and Klusman, 2002) or an average of ~3 Tg CH<sub>4</sub>/yr. Finally, the world ocean ridge system emits negligible amounts of CH<sub>4</sub> to the oceans, estimated by Welhan and Craig (1983) to be 0.1 Tg/yr, as reported in Judd (2000). The amount of CH<sub>4</sub> reaching the atmosphere from mid-ocean ridges is also likely negligible.

Table 3 summarizes CH<sub>4</sub> emissions from various geological sources in Gaia's breath including macro- and micro-seeps, mud volcanoes, gas hydrates, magmatic volcanoes, geothermal areas, and mid-ocean ridges. These emission rates range from 44 to 48 Tg CH<sub>4</sub>/yr, depending on the role that emissions from gas hydrate may play. The values fall within the range of geological emissions of 40–60 Tg CH<sub>4</sub>/yr as recently proposed by Etiope (2004).

Table 3  
Summary of estimates of CH<sub>4</sub> emissions to the atmosphere from various geological sources

Geological source	Flux (Tg CH <sub>4</sub> /yr)
Natural macro-gas seeps	25
Mud volcanoes	5
Micro-seeps of natural gas	7
Gas hydrate	<4
Magmatic volcanoes	4
Geothermal areas	3
Mid-ocean ridges	0
Total	44 (w/o gas hydrate) 45 (w/ gas hydrate, thermogenic CH <sub>4</sub> ) 48 (w/ gas hydrate, thermogenic and microbial CH <sub>4</sub> )

### 5. Adjusted global CH<sub>4</sub> budget; implications for climate change

If it is agreed that IPCC (2001) encompasses the latest consensus thinking concerning the global CH<sub>4</sub> budget (Fig. 1), then the newly identified geological source strength of 45 Tg CH<sub>4</sub>/yr must be accounted for within the total global source strength of ~600 Tg CH<sub>4</sub>/yr. Of this 600, 110 Tg CH<sub>4</sub>/yr is attributed to the anthropogenic use of fossil fuel in the mining of coal and the production of petroleum (Fig. 1). This exploitation of fossil fuels results in fossil CH<sub>4</sub>, and a 110 Tg CH<sub>4</sub>/yr emission rate of old CH<sub>4</sub> is needed to offset the microbial or young CH<sub>4</sub> (490 Tg CH<sub>4</sub>/yr) and to balance the carbon isotopic constraints of the CH<sub>4</sub> budget for both <sup>14</sup>C and <sup>13</sup>C (Fig. 7). Because geologically sourced CH<sub>4</sub> is also old and contributes ~45 Tg CH<sub>4</sub>/yr to the atmosphere, this constant source of old CH<sub>4</sub> has to be part of the global CH<sub>4</sub> budget. Thus, the 110 Tg/yr fossil fuel emission rate is constrained to satisfy the remainder of the total budget, and the 45 Tg/yr rate for geologically-sourced old CH<sub>4</sub> must be part of the 110 Tg/yr. Therefore, the amount of CH<sub>4</sub> emission attributed to fossil-fuel usage should be reduced by 45 Tg

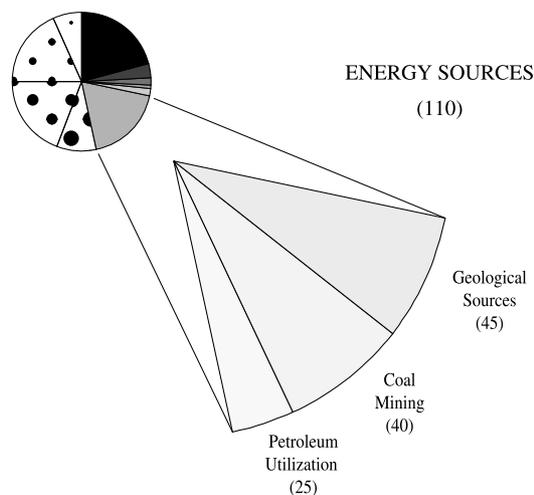


Fig. 7. Diagram of the adjusted global atmospheric budget (Fig. 1) for geologically-sourced CH<sub>4</sub>. Units in Tg CH<sub>4</sub>/yr.

CH<sub>4</sub>/yr, leaving 65 Tg CH<sub>4</sub>/yr to be assigned to the exploitation of fossil fuels. The 65 Tg CH<sub>4</sub>/yr needs to be partitioned between coal mining activities and petroleum production activities, and we suggest, as an approximation, that 40 Tg CH<sub>4</sub>/yr be assigned to coal mining and 25 Tg CH<sub>4</sub>/yr to petroleum production. If this assignment is correct, then the yearly emissions attributed to petroleum exploitation are reduced by a factor of 2 from previous estimates of ~45 Tg CH<sub>4</sub>/yr, whereas estimates of emissions from coal mining remain about the same as determined by Lelieveld et al. (1998). This assignment seems reasonable, although speculative, because coal utilization is increasing internationally and coal-bed CH<sub>4</sub> is an emerging energy source. Thus, CH<sub>4</sub> emissions from coal mining are not adjusted. On the other hand, in petroleum transmission and production, there has been a reduction in the flaring of excess CH<sub>4</sub>, and transmission facilities are becoming more efficient. Thus, the assigned CH<sub>4</sub> emissions from this source have been reduced.

The CH<sub>4</sub> emissions from gas hydrate present a special case. Although gas hydrate is composed of fossil or old CH<sub>4</sub>, most of this CH<sub>4</sub> is microbially generated and has a light carbon isotopic composition of ~−60‰ (Kvenvolden, 1995). In contrast, the CH<sub>4</sub> from other geological sources is produced by thermogenic processes, resulting in old CH<sub>4</sub> with heavy carbon isotopic compositions between −20 and −52‰. The assumption here is that all isotopically heavy CH<sub>4</sub> is coming from thermogenic rather than partially oxidized microbial sources. Satisfaction of the current CH<sub>4</sub> global budget requires CH<sub>4</sub> that is both old and isotopically heavy. Thus, CH<sub>4</sub> from gas hydrate appears to be a minor factor with a source strength of <4 Tg CH<sub>4</sub>/yr in the current global CH<sub>4</sub> atmospheric budget, from both quantitative and carbon isotopic viewpoints. On the other hand, massive release of gas-hydrate CH<sub>4</sub>, as postulated by Dickens et al. (1995) and Kennett et al. (2002), could alter the overall CH<sub>4</sub> budget by adding isotopically light carbon to the ocean/atmosphere system. Such massive injections of CH<sub>4</sub> from gas hydrate may have affected global climates in the past, but much of the CH<sub>4</sub> from geological sources in today's global budget is part of the atmospheric background, having little if any affect on present changes in global climate. Any massive release of gas-hydrate CH<sub>4</sub> in the future might influence global climate, but the extent of this influence cannot yet be predicted, given the current state of knowledge.

## 6. Conclusions

Except for CH<sub>4</sub> from gas hydrate, CH<sub>4</sub> from geological sources is not considered in current estimates of the global atmospheric CH<sub>4</sub> budget. Instead, all of the fossil CH<sub>4</sub> (110 Tg/yr) needed to balance the global budget quantitatively and isotopically is attributed to fossil-fuel utilization. This assessment needs to be revised to recognize

the contributions of geologically-sourced CH<sub>4</sub> from macro-seeps, micro-seepage, mud volcanoes, magmatic volcanoes, geothermal areas, and mid-ocean ridges. We conservatively estimate that the amount of geologically sourced CH<sub>4</sub> entering the atmosphere totals 45 Tg CH<sub>4</sub>/yr. Thus, estimates of yearly emissions from fossil-fuel utilization need to be reduced by this amount, leaving 65 Tg CH<sub>4</sub>/yr to be partitioned between the fossil-fuel usages of coal mining and petroleum exploitation. We suggest that a reasonable partition is 40 Tg CH<sub>4</sub>/yr for coal mining and 25 Tg CH<sub>4</sub>/yr for petroleum utilization. This means that estimates of emissions from petroleum usage are reduced by about a factor of 2 and estimates for coal-mining emissions remain about the same as previously reported. The effect of geologically-sourced CH<sub>4</sub> on current global climate change is considered to be minimal. However, massive releases of gas-hydrate CH<sub>4</sub> could alter the overall CH<sub>4</sub> budget by adding isotopically light carbon to the ocean/atmosphere system. Such massive injections of CH<sub>4</sub> from gas hydrate may have affected global climates in the past, and any massive releases of gas-hydrate CH<sub>4</sub> in the future might influence global climate, although the extent of this influence cannot yet be predicted, given current understanding.

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